EDGEWOOD

CHEMICAL BIOLOGICAL CENTER

U.S. ARMY RESEARCH, DEVELOPMENT AND ENGINEERING COMMAND

ECBC-TR-431

POTENTIAL USAGE OF AQUEOUS ALUM
FOR DECOMPOSITION OF CHEMICAL WARFARE AGENTS
PART 2: REACTIONS WITH VX AND QL

Daniel J. Williams

SAIC-APG SITE

Vicky L. H. Bevilacqua

RESEARCH AND TECHNOLOGY
DIRECTORATE

William R. Creasy
David J. McGarvey

EAI CORPORATION
Abingdon, MD 21009-2304

Jeffrey S. Rice

RESEARCH AND TECHNOLOGY
DIRECTORATE

Christopher L. De Leon
Melanie J. Sanders

KENNESAW STATE UNIVERSITY
Kennesaw, GA 30144-5591

H. Dupont Durst

RESEARCH AND TECHNOLOGY
DIRECTORATE

May 2006

Kennesaw State UNIVERSITY

SAIC®
An Employee-Owned Company

EAI
A Registered ISO-9001 Company

ABERDEEN PROVING GROUND, MD 21010-5424

20060922020

Disclaimer

The findings in this report are not to be construed as an official Department of the Army position unless so designated by other authorizing documents.

REPORT DOCUMENTATION PAGE

1. REPORT DATE *(DD-MM-YYYY)*	2. REPORT TYPE	3. DATES COVERED *(From - To)*
XX-05-2006	Final	May 2004 - Nov 2004

4. TITLE AND SUBTITLE

Potential Usage of Aqueous Alum for Decomposition of Chemical Warfare Agents
Part 2: Reactions with VX and QL

5a. CONTRACT NUMBER
DAAD13-03-D0017

5b. GRANT NUMBER

5c. PROGRAM ELEMENT NUMBER

6. AUTHOR(S)

Williams, Daniel J. (SAIC/Kennesaw State University); Bevilacqua, Vicky L. H. (ECBC);
Creasy, William R.; McGarvey, David J. (EAI); Rice, Jeffrey S. (ECBC);
De Leon, Christopher L.; Sanders, Melanie J.; McKinney, Bradley J. (Kennesaw State
University); and Durst, H. Dupont (ECBC)

5d. PROJECT NUMBER
10601384 BPO

5e. TASK NUMBER

5f. WORK UNIT NUMBER

7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES)
DIR, ECBC, ATTN: AMSRD-ECB-RT-PC, APG, MD 21010-5424
SAIC, Abingdon, MD 21009
EAI Corporation*, Abingdon, MD 21009-2304
Kennesaw State University, 1000 Chastain Road, MS 1023,
Kennesaw, GA 30144-5591

8. PERFORMING ORGANIZATION REPORT
ECBC-TR-431

9. SPONSORING / MONITORING AGENCY NAME(S) AND ADDRESS(ES)

10. SPONSOR/MONITOR'S ACRONYM(S)

11. SPONSOR/MONITOR'S REPORT NUMBER(S)

12. DISTRIBUTION / AVAILABILITY STATEMENT
Approved for public release; distribution is unlimited.

13. SUPPLEMENTARY NOTES
*Now part of Science Applications International Corporation (SAIC), Abingdon, MD 21009.

14. ABSTRACT
O-ethyl-S-[2-(diisopropylamino)ethyl] methylphosphonothiolate (VX) and its precursor, O-ethyl-O'-(2-isopropylaminoethyl) methylphosphonite (QL), were treated with aqueous aluminum sulfate (alum), sodium aluminate, or mixtures of the two. The mixtures were prepared by combining varying volumes of the aqueous salts to give buffered solutions (pH 2-12). Reactions were tracked using phosphorus-31 nuclear magnetic resonance (NMR) and gas chromatography/mass spectrometry (GC/MS). The NMR spectra of QL hydrolysate showed three broad peaks that are speculated to be different aluminum complexes of methylphosphinic acid based on proton coupling studies. Acidic alum and alum buffers removed anywhere from 50 to 70% VX within the first 20 min from reaction mixtures in NMR tubes. No evidence of EA-2192 production was observed, and the main hydrolysis product, ethyl methylphosphonic acid, was also precipitated from solution. Studies with larger stoichiometric excesses of alum relative to agent are currently under way, but it appears that acidic alum and alum buffers may provide an effective alternate method for the destruction of VX and QL.

15. SUBJECT TERMS

Alum	Buffered alum	QL	VX	Nuclear magnetic resonance
Aluminum sulfate	Decontamination	NMR		

16. SECURITY CLASSIFICATION OF:			17. LIMITATION OF ABSTRACT	18. NUMBER OF PAGES	19a. NAME OF RESPONSIBLE PERSON
a. REPORT	b. ABSTRACT	c. THIS PAGE	UL	17	Sandra J. Johnson
U	U	U			**19b. TELEPHONE NUMBER** *(include area code)* (410) 436-2914

Blank

PREFACE

The use of either trade or manufacturers' names in this report does not constitute an official endorsement of any commercial products. This report may not be cited for purposes of advertisement.

This report has been approved for public release. Registered users should request additional copies from the Defense Technical Information Center; unregistered users should direct such requests to the National Technical Information Service.

Acknowledgments

Blank

CONTENTS

FIGURES

TABLES

POTENTIAL USAGE OF AQUEOUS ALUM
FOR DECOMPOSITION OF CHEMICAL WARFARE AGENTS
PART 2: REACTIONS WITH VX AND QL

1.   INTRODUCTION

The destruction of chemical warfare agents (CWA's), particularly O-ethyl-S-[2-(diisopropylamino)ethyl] methylphosponothiolate (VX), has been the focus of many articles in the popular media and in professional news journals such as Chemical and Engineering News.[1,2,3] One of the main concerns with CWA detoxification is the potential threat that hydrolysis by-products may be recovered for reuse in CWA synthesis.[2] There is also concern about the transport, treatment, and disposal of hydrolysate among environmental groups and citizen stake-holders in states where the proposed destruction is to occur.[2] Truly environmentally friendly means of detoxifying CWAs have yet to be developed, and the possibility of using alum and alum mixtures may be one feasible attractive alternative. Trapping hydrolysis by-products in a coagulant floc can make them very difficult to recover.

Municipal water treatment facilities have a long history of using alum (aluminum sulfate) and alum mixtures as coagulants in the purification and finishing of drinking water. Our previous studies have shown alum and alum buffered by the addition of sodium aluminate to be effective in the destruction of G agents, particularly pinacolyl methylphosphonofluoridate (GD).[4] The work we did with VX, however, was inconclusive owing to the lack of internal standards to determine the initial amount of agent loss upon treatment. Rate studies without controls seemed to indicate that VX was susceptible to alum treatment, and literature precedent indicated that solid state Al_2O_3 nano-particles were also effective to a degree in destroying VX.[5] Furthermore, the question arose as to whether alum and alum buffers would be useful in destroying the phosphorus-based precursor of VX, O-ethyl-O'-[(2-isopropylamino)ethyl] methylphosphonite (QL).

Hydrolysis kinetics have been studied for a large number of CWAs,[5,6,7] and all indications are that the rates are pH dependent. The same is true for QL.[8] The pH of alum and alum mixtures can be adjusted from strongly acidic to strongly basic depending on concentrations and proportions of components, which should allow for some control over hydrolysis reaction rates. Additionally, the use of buffered systems is attractive because it has been demonstrated that hydrolysis of some CWA's results in a change of pH in the reaction mixture thus altering the rate of hydrolysis.[5] Another attractive feature of the treatment process relies on the fact that many aluminum phosphate complexes are extremely insoluble so hydrolysis of agent and precipitation of by-products could be achieved as indicated above.

Herein, the second installment of an investigation of the potential of using alum and alum mixtures for the destruction of VX and QL is reported.

2.   EXPERIMENTAL PROCEDURES

2.1   Materials.

Both VX and QL were obtained from the Chemical Transfer Facility, Aberdeen Proving Ground, MD. The purity of both agents was deemed satisfactory for study based on [31]P Nuclear Magnetic Resonance (NMR) spectra obtained in $CDCl_3$ as described below. All other chemicals were used as commercially obtained (Aldrich and subsidiaries) without further purification. Solutions of 1.0 M $Al_2(SO_4)_3$ and 1.0 M $NaAlO_2$, were prepared with deionized water. Unless otherwise noted, all reactions were carried out in 5 mm NMR tubes (507-PP Wilmad Glass, Inc.) in total volumes ranging from 700 to 1000 μL. The total volumes include D_2O added as a lock solvent to give 3 - 30% D_2O by volume.

2.2   Alum Buffer Studies.

Buffer pH values from using 1.0 M reagents were measured for solutions prepared by mixing 1.0 M aluminum sulfate (alum) and 1.0 M sodium aluminate solutions in 5 mL vials. All test solutions were brought up to a constant total volume of 2.0 mL, and the pH was measured using a Scientific Instruments IQ150 pH Meter fitted with solid state pH probe with internal reference. Volume fractions of alum relative to the sum of alum plus sodium aluminate volumes were then computed and plotted against pH. Table 1 shows the final molar concentration of each component after mixing. The estimated error in reported pH values is ±0.5 units.

2.3   ^{31}P NMR Spectral Data.

All NMR experiments reported are ^{31}P detected, proton inverse gated decoupled. The NMR experiments were collected on samples prepared directly in NMR tubes as described above using a Bruker AVANCE 300 MHz NMR spectrometer fitted with a 5 mm QNP probe. All spectra were referenced to external H_3PO_4 (1% (v/v) in D_2O; 0 ppm). Test solutions were prepared by adding from 20 to 40 μL agent to NMR tubes already containing D_2O and H_2O. Alum and alum buffers were reacted with simulants and agents in 5 mm NMR tubes as described before.[1] For this work, VX reactions were in doubly-contained NMR tubes and employed 5 μL agent and 500 μL alum solution. Spectra were collected on spinning samples (20 Hz) at 121.4 MHz using eight scans with a 60-sec delay time between scans. Proton decoupling was accomplished by using the WALTZ16 composite decoupling sequence. All reactions were carried out at ambient temperature (21 – 23 °C). Chemical shifts are reported in parts per million (ppm, δ) relative to the external H_3PO_4 standard. The detection limits were 0.1% of initial analyte concentration.

Methylphosphinic acid (MP) derived from decontaminated QL solutions (50 μL, concentration unknown) was treated separately with 5 mL volumes of 1.0 M

$Al_2(SO_4)_3$, alum buffer pH 4, and deionized water as a control. Samples were centrifuged and 700 μL aliquots were used to acquire the ^{31}P-NMR spectra.

2.4   Reaction Rate Experiments.

Time course experiments were conducted on varying amounts of QL using only acid buffers. Experiments were conducted on QL at pH = 2, 3, and 4. Malathion and diazinon were treated with pH 4 buffer. The VX reactions were carried out with four different alum solutions: 1.0 M $Al_2(SO_4)_3$, 1.0 M $NaAlO_2$, pH 4 buffer, and pH 3 buffer. The VX results are reported as percent of original concentration based on comparison with external standards. In the case of QL, concentrations are reported as integration areas. Reactions on VX and QL were monitored with ^{31}P-NMR over various time frames ranging from < 30 min to several days. Some studies used hexamethylphosphoramide (HMPA) as an internal standard.

3.   RESULTS AND DISCUSSION

3.1   Alum Buffer Studies.

The 1.0 M solutions were selected for use rather than the saturated solutions used for the previous study.[4] As shown in Table 1 and Figure 1, pH values for buffers prepared from 1.0 M solutions were in agreement with our earlier observations. Both VX and QL tend to be more soluble in acidic solution, which is another reason for choosing 1.0 M solutions over buffers derived from saturated solutions. Because of lock solvent (D_2O) already present in the NMR tube prior to mixing, the actual $Al_2(SO_4)_3$ molarity is < 1.0 M. However, for simplicity, when unbuffered aluminum sulfate is used, it will be noted as 1.0 M.

Table 1. Final Molar Concentrations of $Al_2(SO_4)_3$ and $NaAlO_2$ in Buffer Solutions

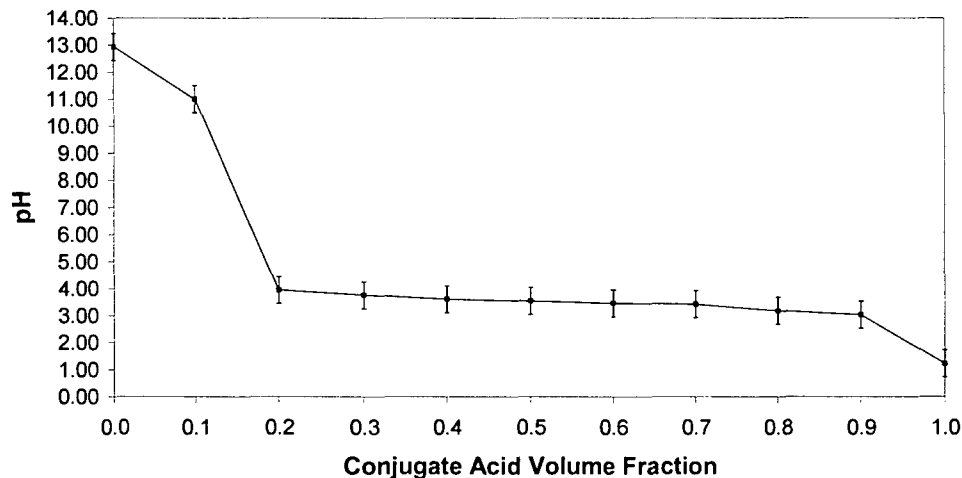| [$Al_2(SO_4)_3$]	[$NaAlO_2$]	pH	[$Al_2(SO_4)_3$]	[$NaAlO_2$]	pH
0.00 M	0.50 M	12.9	0.25 M	0.25 M	3.6
0.05 M	0.45 M	11.0	0.30 M	0.20 M	3.5
0.10 M	0.40 M	4.0	0.35 M	0.15 M	3.4
0.15 M	0.35 M	3.8	0.40 M	0.10 M	3.2
0.20 M	0.30 M	3.6	0.45 M	0.05 M	3.0
			0.50 M	0.00 M	1.2

Figure 1. Alum Buffer pH Values as a Function of Volume Fraction for Buffers Prepared from Dilutions of 1.0 M Alum/Sodium Aluminate Stock Solutions

3.2 QL Studies.

The QL reacts within 20 min when exposed to 1.0 M $Al_2(SO_4)_3$ or alum buffers at pH 2, 3, and 4. No QL peak was observed in the ^{31}P-NMR spectra, but the peaks from two hydrolysis products, ethyl methyl phosphinate (EMP, δ 45.7 ppm) and diisopropylaminoethyl methyl phosphinate (DMP, δ 43.3 ppm), were seen. These two peaks slowly decreased in intensity while three broad peaks discussed further in the section below grew in intensity. Table 2 shows the half-lives for EMP and DMP as a function of pH.

Table 2. Half-lives (hr) of QL Hydrolysis Products, DMP and EMP

Treatment Solution	EMP	DMP
1.0 M $Al_2(SO_4)_3$ (pH = 1.2)	3.0	15
Alum Buffer pH = 2	2.0	30
Alum Buffer pH = 3	1.0	10
Alum Buffer pH = 4	1.0	20

The final products are suspected to be three different aluminum complexes of methyl phosphinic acid (MP), with broad peaks centered at δ 33.7, 23.1, and 21.7 ppm. Ester products were assigned by comparison with published chemical shifts[8], and all phosphinic acid derivatives were confirmed with proton coupled ^{31}P-NMR spectra. Reaction rates were in agreement with literature observations[8] to the extent

10

that EMP disappears more rapidly than DMP. The EMP half-life was inversely proportional to pH, a trend which is also consistent with the observations of Verweij, et al. [8] No clear trend with respect to pH for DMP was observed.

One method of destroying QL has been to employ a 0.3% NaOH solution at 38 ^{O}C for hydrolysis. The QL is not very soluble in base, and the resultant biphasic system can affect the kinetics. The alum treatment described above was so rapid that no evidence of QL was found in the initial NMR spectra thus making rate studies for the disappearance of QL nearly impossible.

The identities of the MP aluminum complexes are still under investigation. Figure 2a shows a ^{31}P-NMR spectrum of an MP reaction mixture in unbuffered $Al_2(SO_4)_3$ (~1.0 M). For comparison, Figure 2b shows a control spectrum of MP in water, and Figure 2c shows a QL reaction mixture in pH 3 alum buffer after 3 days. Except for the impurity peak and the residual EMP peak, the treated QL spectrum closely correlates to the reaction mixture shown in Figure 2a.

Experiments on MP alone with a large molar excess of alum and alum buffer (pH 4), followed by centrifugation, showed virtually all of the MP was removed from solution as evidenced by the ^{31}P-NMR spectrum (Figure 2d). Additional proof that the peaks observed in Figures 2b and 2c are MP complexes is seen in Figure 2e which shows a proton coupled spectrum of the QL reaction mixture in buffer pH 3 taken 3 days after initial treatment. All three MP peaks and the EMP peak show the characteristic splitting arising from ^{31}P-^{1}H coupling expected for methylphosphinic acid (J_{PH} = 560 Hz). Figure 3 shows the reaction time profile in pH 2 alum buffer.

3.3 VX Studies.

Our previous study investigated the effect of alum and buffered alum solutions on VX, but the results were inconclusive since no external standards were used to assess initial destruction.[4] Our results did, however, indicate that alum removed VX from aqueous solutions over time, but the initial rates were not determined. In this study, we repeated the VX experiments treating VX with 1.0 M $Al_2(SO_4)_3$, pH 4 alum buffer, and 1.0 M $NaAlO_2$. Table 3 shows the initial loss rates in % of original concentration based on an external standard, and the half life of residual VX in days.

As can be seen in Table 3, 1.0 M $NaAlO_2$ was the most successful in terms of removing VX from solution, but further studies were abandoned due to the formation of the very toxic hydrolysis product sodium S-[2-(diisopropyl-amino)-ethyl] methylphosphonothiolate (EA-2192), as seen in Figure 4. Chemical shift assignments were based on literature values.[9] The acidic buffered alum solution was comparable to 1.0 M $Al_2(SO_4)_3$ in reducing the concentration of VX initially, but as Figure 5 shows, it removes all phosphorus hydrolysis products including ethyl methylphosphonic acid (EMPA) from solution. Furthermore, there was no evidence for the production of EA-2192.
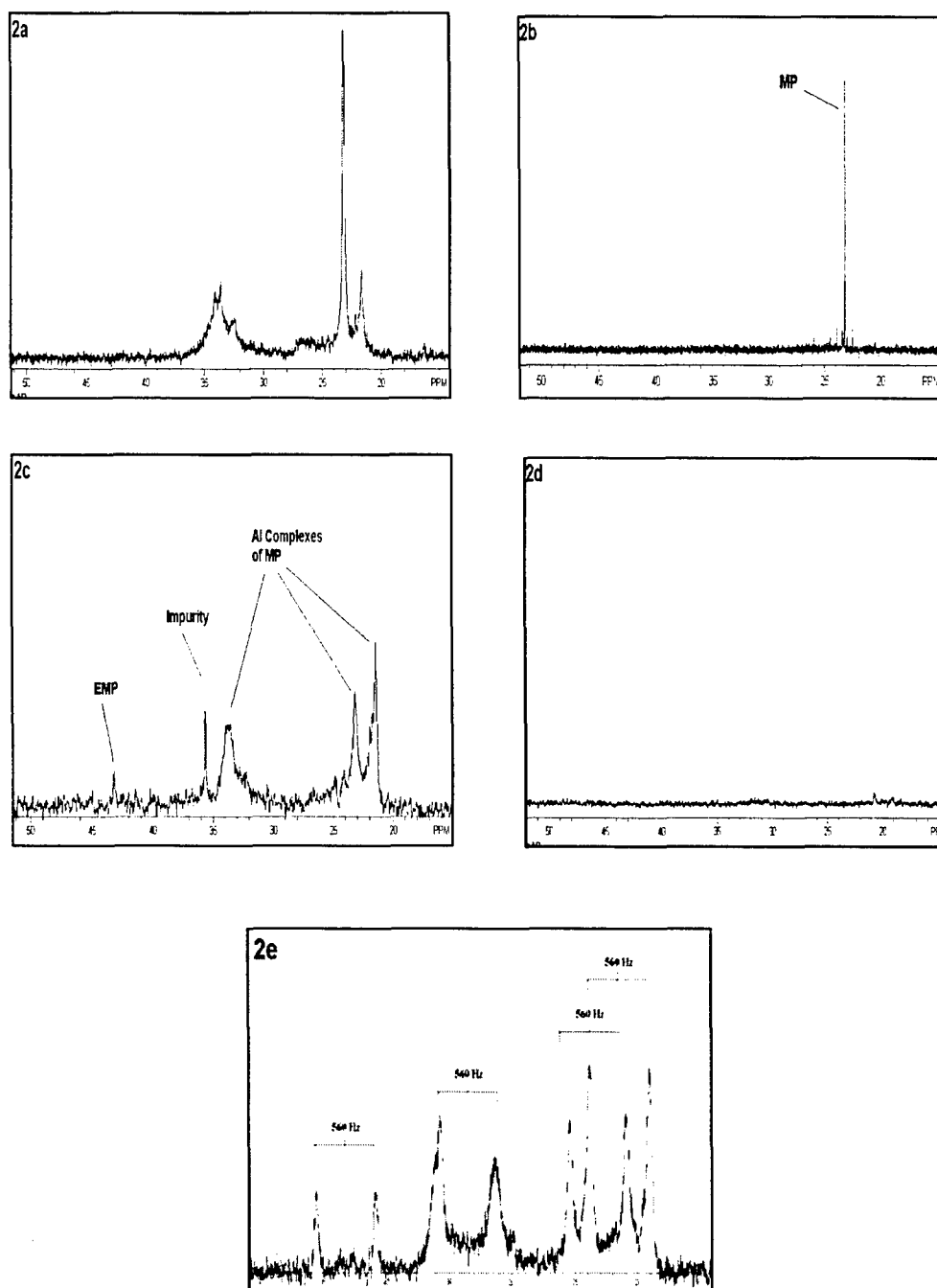
Figure 2. ^{31}P NMR Spectra of MP and QL Reactions: a) MP Reaction Mixture
in Unbuffered $Al_2(SO_4)_3$ (~1.0 M) Compared to b) Untreated MP;
c) QL Reaction Mixture in pH 3 Alum Buffer After 3 days; d) Reaction
Mixture of MP Treated with Large Molar Excess of $Al_2(SO_4)_3$;
e) (Proton Coupled) QL Reaction Mixture in pH 3 Alum Buffer
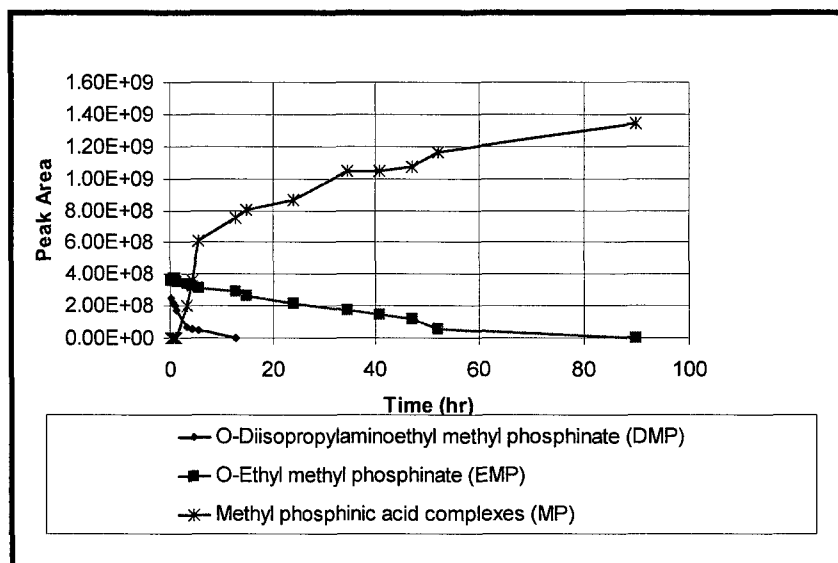After 3 Days.

Figure 3. QL Reaction Time Profile in pH 2 Alum Buffer

Table 3. Initial Loss Rates and Half-lives (Days) of Residual VX
After Treatment with Alum Solutions

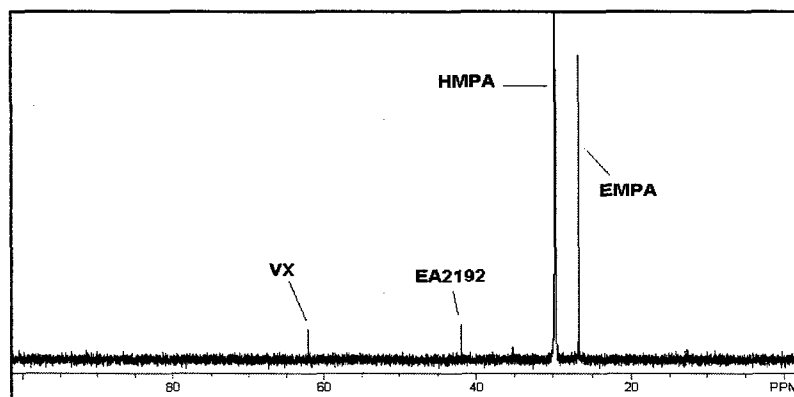| Treatment Solution	Initial Loss	Remaining VX Half Life
1.0 M $Al_2(SO_4)_3$	66.6%	34
pH 4 Alum Buffer	64.2%	5
1.0 M $NaAlO_2$	97.3%	Not measured

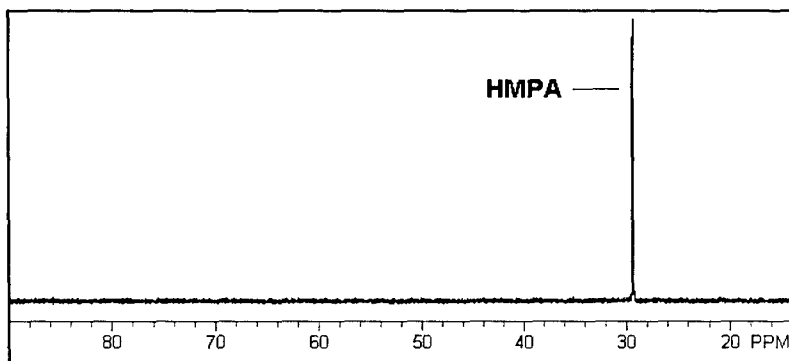Figure 4. ^{31}P NMR Spectra of VX Treated with 1.0 M $NaAlO_2$ (pH ~12.5)

Figure 5. VX Treated with pH 4 Alum Buffer After 12 days

Time course experiments with VX in 1.0 M $Al_2(SO_4)_3$ showed an initial loss of 66.6% of the original concentration, but a half-life of 34 days for the remaining VX. The buffered alum solution (pH 4) removed VX from solution more rapidly even though it had a slightly smaller initial reduction percentage. Figure 6 shows the loss of VX over time after the initial loss as determined by comparison with external controls. In all cases using acidic conditions, the principle hydrolysis product, ethyl methylphosphonic acid (EMPA), is taken out of solution (Figure 5). If hydrolysis proceeds further, a secondary hydrolysis product, methylphosphonic acid (MPA), is also formed.[10] Aluminum complexes of EMPA and MPA are soluble at near neutral pH but are insoluble at higher proton concentrations as observed by Wagner, et al.[10]
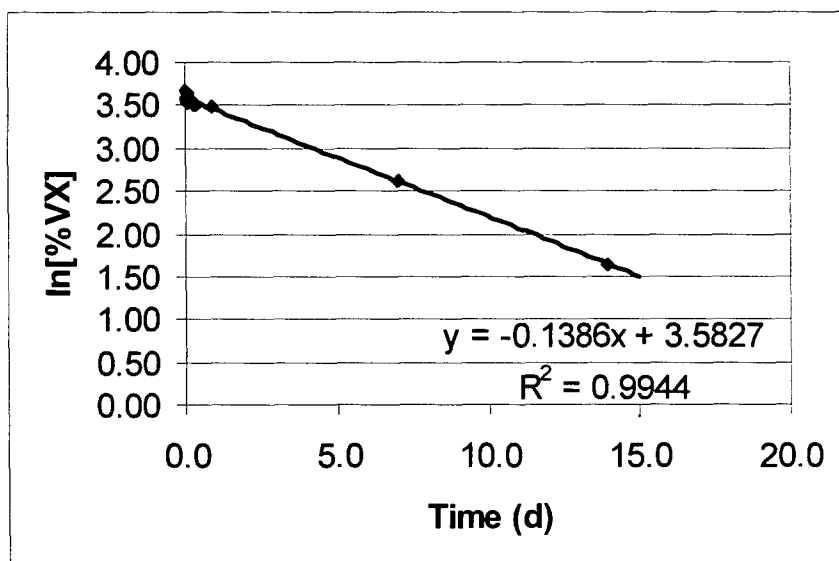

Figure 6. Loss of VX Over Time After Initial Reaction in Buffered Alum Solution at pH 4 (ln[%VX] vs. time in days), $t_{1/2}$ = 5 Days.

14

4.   CONCLUSIONS AND FURTHER STUDY

Alum treatment appears to be a very effective method for the destruction of O-ethyl-O'-[(2-isopropylamino)ethyl] methylphosphonite (QL) and O-ethyl-S-[2-(diisopropylamino)ethyl] methylphosponothiolate (VX). The process is attractive for QL because alum buffers destroy the QL almost instantaneously and much more rapidly than basic methods. Due to greater solubility of QL in acid, no biphasic mixtures are encountered as in basic methods of hydrolysis. As for hydrolysis products, ethyl methyl phosphinate (EMP) and diisopropylaminoethyl methyl phosphinate (DMP) ultimately revert to methylphosphinic acid (MP) at varying rates depending on pH, and the aluminum methylphosphinic acid complexes are completely removed from solution due to low solubility.

Alum buffer at pH 4 appears to be most effective for initial destruction of VX and subsequent removal of ethyl methylphosphonic acid (EMPA) and methylphosphonic acid (MPA) from solution without production of S-[2-(diisopropyl-amino)-ethyl] methylphosphonothiolate (EA-2192). We are looking at increasing the efficiency of the reaction through various engineering processes such as reaction column experiments (~10 mL solid alum bed volume) with alum present at greater than or equal to 100-fold excess over agent and saturated alum as the eluent.

As mentioned above, our earlier studies have shown success in the removal of other organophosphorus agents such as GD[4], and we will be further investigating other G agents as well as alum treatment of mustards. Alumina has been shown to speed up the destruction of HD[10], and we will be looking into the possibilities of applying alum and alum buffers to the destruction and removal of hydrolysis products of mustards.

Blank

LITERATURE CITED

1. Ember, L.R. Destroying VX. *C&E News.* **2004,** *82(15),* pp 28-30.

2. Ember, L.R. Destroying Weapons. *C&E News.* **2003,** *81(35),* pp 26-27.

3. Ember, L.R. VX Nerve Gas Disposal at Newport, Ind., to Begin in Fall. *C&E News.* **2004,** *82(39),* p 18.

4. Williams, D.J.; Bevilacqua, V.L.H.; Creasy, W.R.; Maguire, K.J.; McGarvey, D.J.; Brevett, C.A.S.; Rice, J.S.; Durst, H.D. Investigation of Alum Mixtures for the Removal and Decontamination of V- and G- Type Chemical Warfare Agents from Aqueous Solutions. In *Proceedings of the 2003 Joint Service Scientific Conference on Chemical and Biological Defense Research,* 17-20 November 2003; Berg, D.A., Compiler; U.S. Army Edgewood Chemical Biological Center: Aberdeen Proving Ground, MD, 2005; UNCLASSIFIED Report (AD-M001851).

5. Yang, Y.; Baker, J.A.; Ward, J.R. Decontamination of Chemical Warfare Agents. *Chem. Rev.* **1992,** *92,* pp 1729-1743.

6. Yang, Y.; Szafraniec, L.L.; Beaudry, W.T.; Rohrbaugh, D.K.; Procell, L.R.; Samuel, J.B. Autocatalytic Hydrolysis of V-Type Nerve Agents. *J. Org. Chem.* **1996,** *61,* pp 8407-8413.

7. Wagner, G.W.; O'Connor, R.J.; Procell, L.R. Preliminary Study on the Fate of VX in Concrete. *Langmuir.* **2001,** *17,* pp 4336-3431.

8. Verweij, A.; Dekker, W.H.; Beck, H.C.; Boter, H.L . Hydrolysis of Some Methylphosphonites and Methylphosphinates. *Anal. Chim. Acta* **1983,** *151,* pp 221-225.

9. Yang, Y.; Szafraniec, L.L.; Beaudry, W.T.; Rohrbaugh, D.K. Oxidative Detoxification of Phosphonothiolates. *J. Amer. Chem. Soc.* **1990,** *112,* pp 6621-6627.

10. Wagner, G.W.; Procell, L.R.; O'Connor, R.J.; Munavalli, S.; Carnes, C.L.; Kapoor, P.N.; Klabunde, K.J. Reactions of VX, GB, GD, and HD with Nanosize Al_2O_3. Formation of Aluminophosphonates. *J. Amer. Chem. Soc.* **2001,** *123,* pp 1636-1644.